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Influence of preparation conditions onto the characteristics of the titania and silica templates

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Titania and silica templates were successfully synthesized by one step anodization process. The morphologies and the characteristics of the as-synthesized samples were systematically investigated by SEM analysis. The influence of the applied potential value on the diameter of the titania and silica template was discussed. The obtained templates can be used for the nanowires electrodeposition, arrays of NiFe alloys nanowires have been synthesized by electrodeposition into the pores of titania and silica templates.

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1. Introduction

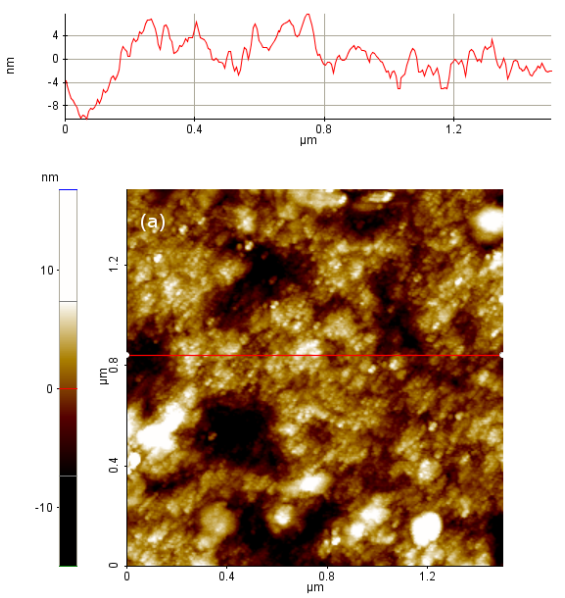
In the recent years, the development of novels methods for the preparations of "nano" structures has been widely studied because of the possibility to use these structures at the fabrication of the miniaturized integrated circuits. Also, the physical proprieties of nano-materials are different from bulk materials properties. Many kinds of noble metals, magnetic metals and magnetic alloys nanowires have been prepared by electrodeposition into the nanopores of oxide templates [1, 2, 3]. In the past years, many methods have been developed to control the dimension and the morphology of the different templates: alumina, titania and silica. The most studied template is the alumina template which can be easily obtained by two-steps anodization process [4]. The influence of the anodic conditions on the self ordered growth of alumina nanopores was extensively explored and the results are the object of the numerous papers [5, 6, 7]. The data presented in the literature show that the anodic aluminum template can also be prepared by one-step anodization process. In this case, prior to the anodization the aluminum surface must be intended and the formed depressions served as initiation sites for the pores generation at the initial stage of anodization [8]. The anodic aluminum oxide was proposed to be used for various applications, like for example: template for the nanowires electrodeposition [9, 10, 11], evaporation mask [12], photonics and optoelectronics [13].

Recently, the scientifics has discovered that the self-organized nanoporous structures of other elements, such as titanium [14, 15] and silicon [16, 17], can be formed under optimized electrochemical conditions. These porous oxides can be used for the electrochemical nanowires preparation [18, 19,20]. The data presented in the literature show the influence of the anodization temperature or the electrolyte chemical composition on self-ordered growth of titanium or silicon oxide nanopores [21, 22]. However, the data concerning the influence of the applied voltage onto the characteristics of the titania or silica templates presented in the literature are not always conclusive.

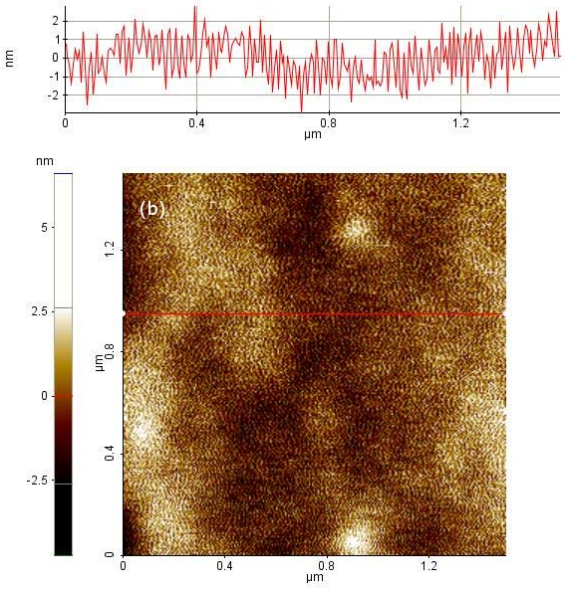
2. Experimental

The titania and silica templates were prepared by anodization process starting with titanium foil (99.5%), 0.25 mm thick provided by Alfa Aesar and p-type silicon wafers (resistivity: 0.1 – 0.14 Ωcm) respectively. Prior to the anodization, the titanium foil was submitted to a mechanically polishing process using diamond (particles size – 3 μm) and Syton (particles size – 20 nm). The role of this step is to obtain a very smooth titanium surface. The surface was verified by atomic force microscopy (AFM) and haute resolution scanning electron microscopy (HR-SEM) measurements. The surface roughness measured with Atomic Force Microscopy (AFM) is about 40 nm (Fig. 1a). Because the silicon wafers has a very smooth surface (Fig. 1b) prior to the anodization process, we just degreased the surface with acetone and washed several times with distilled water.

The next step of the template preparation is the anodization process. This step was performed in hydrofluoric acid aqueous solution for the titanium foil and in hydrofluoric acid in ethanol for the silicon wafers. The surface of the obtained samples was analyzed by HR-SEM using a Carl Zeiss Neon ESB microscope.



a



b

Fig. 1. AFM Topographically image of the polished titanium foil surface (a); AFM Topographically image of the silica wafers surface (b).

3. Results and discussions

Fig. 2 shows the HR – SEM micrographs of the anodic titanium oxide obtained in a hydrofluoric acid aqueous solution.

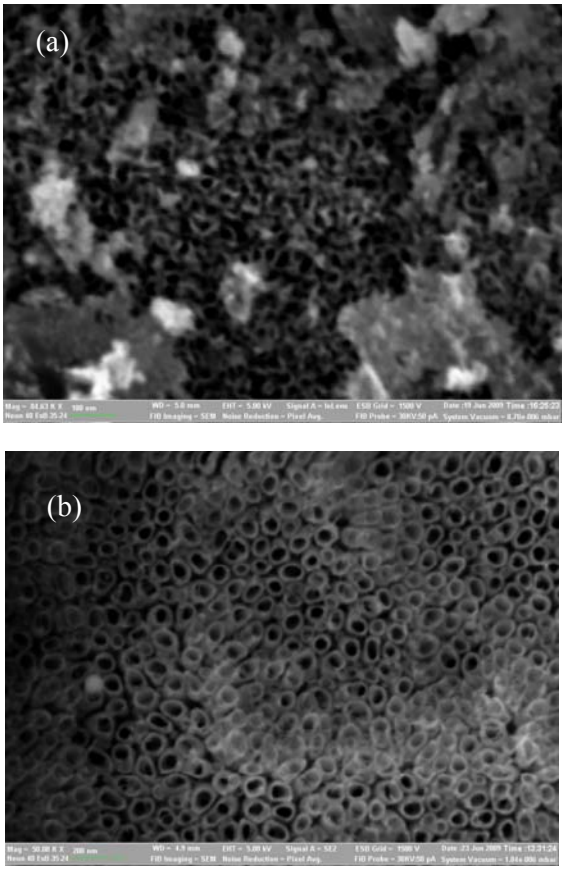


Fig. 2. Top-view HR – SEM micrographs of the self-organized titania template obtained by anodization in 0,5% HF at 20V (a) and 30V (b).

The HR – SEM micrograph analysis of the obtained template surfaces show that the value of the pores diameter of the titania template increases when the anodization voltage increases. We mention the fact that, in all the experiments described here, we kept constant the acid concentration and the anodization temperature and we have varied the anodization voltage. By varying the anodization voltage, we have obtained titania templates with pores diameter 25 nm at 20V, 60 nm at 30V and 150 nm at 40V.

The cross section of the obtained template was also analyzed with the HR – SEM micrograph. These images show the obtained pores are cylindrical and parallel each with another (Fig. 3). The calculate growth rate of the oxide layer is about 0,25 µm/h.

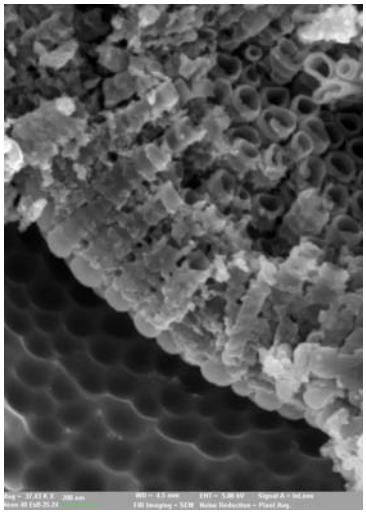


Fig. 3. Cross section HR-SEM images of the tiatania template obtained by anodization process in 0,5% HF at 40 V.

We also performed anodization of titanium foil by using a 0,5 % hydrofluoric acid solution in sulfuric acid 1M. The template obtained in this electrolyte by applying a voltage of 20 V and at room temperature has a pores diameter of 60 nm (at the same temperature and at the same applied voltage by using a hydrofluoric acid aqueous solution we have obtained titania templates with pores diameters of 25 nm).

Like it was mentioned before, we also prepared silica template by silicon wafers anodization. In this case, the anodization process was conducted in a 15% hydrofluoric acid solution in ethanol. All our experiments were performed at room temperature by varying the anodization voltage between 30 V and 60 V. The obtained templates were characterized by HR-SEM microscopy. The SEM analyses show us the fact that the pore diameter increases with the applied voltage. In Fig. 4 is presented the cross sections of the template obtained at 60 V.

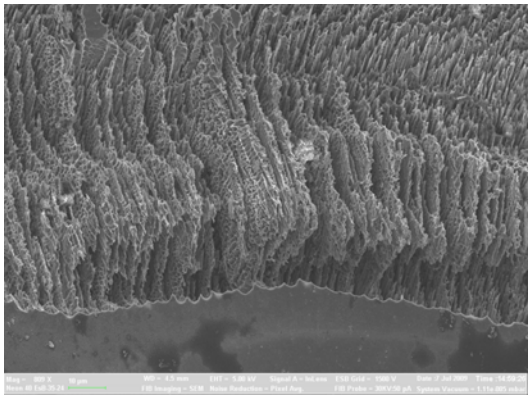


Fig. 4. Cross section HR – SEM micrograph of the self-organized silica templates obtained by anodization process in 15% HF in C_2H_5 – OH at 60 V.

One of the most important applications of these templates is the nanowires preparation inside the nanopores by electrodeposition. In our work we have obtained NiFe alloy nanowires by electrodeposition into the pores of the obtained templates. For performing the electrochemical deposition, we used a three- electrode cell: as reference we used the Saturated Calomel Electrode (SCE), as counter electrode we used Pt foil and as working electrode during the electrochemical deposition we used the titania template which was not detached from the substrate. The applied voltage was controlled during the electrodeposition with a VOLTALAB 10 PGZ 100 potentiostat. NiFe alloys nanowires were growth in aqueous solution of $NiSO_4$ (90g/L), $FeSO_4$ (13.5g/L) and H_3BO_3 (25g/L) by applying a dc voltage of -8V. After the electrodeposition, the titania template filled with NiFe alloys was characterized by HR-SEM. The template filled with NiFe alloys nanowires is presented in Fig. 5.

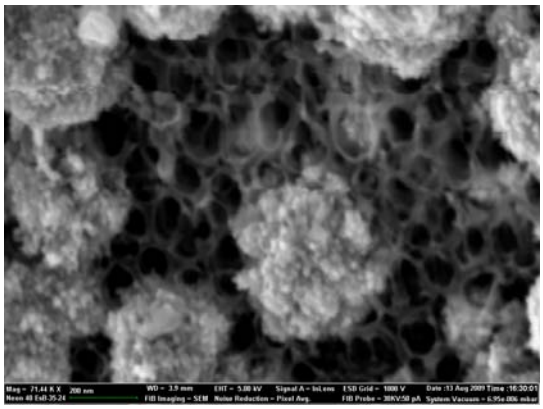


Fig. 5. SEM micrograph of the titania membrane filled with NiFe.

This picture one part of the nanowires are not reach yet the bottom of the pores and another part of the nanowires are growth on to the surface.

4. Conclusions

In conclusion, titania and silica templates have successfully been synthesized by one step anodization process of the titanium foil and silicon conductive wafers. The obtained templates have been investigated by HR – SEM. The results showed that the silica and titania templates have ordered pores arrays. The pores diameter increases with the increase of the applied voltage value. The obtained templates can be used for the nanowires preparation. The arrays of NiFe alloys nanowires have successfully been fabricated by electrodeposition.

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